Notes

Quantitative Studies in Stereochemistry. B. Photochemistry. III. The Ratios of Diastereomeric Pinacols Formed in the Ultraviolet-Promoted Bimolecular Reduction of Selected *para*-Substituted Acetophenones

JACK H. STOCKER, DAVID H. KERN, AND ROY M. JENEVEIN

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

Received June 16, 1967

Previous reports from this laboratory have described the stereochemical consequences of photopinacolizing acetophenone in neutral–acidic[1] and alkaline[2] media. The sharp increase observed in the ratio of *dl*- to *meso*-pinacol formed, from 1.1 to approximately 3.0 when potassium alkoxide was added to the 2-propanol donor–solvent, was attributed to a change in intermediates from dimerizing ketyl radicals to radicals coupling with radical anions. The latter are formed by interaction of ketyl radicals with alkoxide.[2] Since this explanation required hydrogen bonding between species about to couple, an examination of some acetophenones with functional groups of suitable inductive characteristics might offer some additional clarifying data.

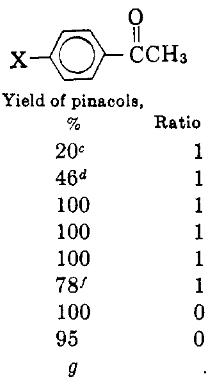
The previous studies were carried out with C^{14}-labeled acetophenone, utilizing isotope dilution techniques. While satisfyingly quantitative, such studies are very time consuming. An nmr analysis of acetophenone and its resultant diastereomerically pure pinacols suggested that adequate quantitative data could be derived from an examination of reaction mixtures by this technique. A comparison of the actual results from both techniques showed excellent agreement. Further advantages of the use of nmr lay in its ability to provide yields of individual pinacols,[3] as well as to permit diastereomeric assignment without tedious isolation and subsequent examination of the individual diastereomers.

Assignment can be based on the observation that in all pairs of pinacols thus far examined of the $(ArRCOH)_2$ type, the hydroxylic proton of the *dl* form appears at lower field strength.[4,5] This observation is readily rationalized after observing models of the more favorable conformations of the various pinacols. The more effective contribution of intramolecular bonding in the *dl* form serves to deshield this proton and causes it to appear downfield from the *meso* isomer. The position appeared to be both concentration and solvent dependent. Yields and ratio calculations[3] based on the broader hydroxylic proton peaks proved somewhat less accurate, although these peaks, in turn, permitted the assignment of the methyl peaks. In those cases where insufficient separation between hydroxylic proton peaks precluded this approach, the methyl proton peak appearing at a higher field strength was attributed to the *dl* isomer. This assignment was based, once again, on an examination of the more favorable conformations. As a result of the relatively higher amount of intramolecular bonding for the *dl* diastereomer, its methyl protons lie above the plane of the phenyl groups and are more effectively shielded than those of the *meso* form, causing them to appear at a higher field strength.

The several acetophenones studied provide a reasonably broad spectrum. The yields and diastereomeric ratios will be found in Table I.

TABLE I

PHOTOPINACOLIZATION[a] OF



Item	X	Time, hr	Yield of pinacols, %	Ratio *dl*/*meso*[b]
1	$-OCH_3$	96	20[c]	1.26
2	$-CH_3$	48	46[d]	1.11
3	-H	24	100	1.09
4	-H	24	100	1.08
5	-H	18	100	1.09[e]
6	-Cl	48	78[f]	1.06
7	$-CF_3$	42	100	0.98
8	$-CF_3$	24	95	0.95
9	-OH	120	*g*	. . .
10	$-NO_2$	120	*g*	. . .

[a] Ketone (1 g) in 10 ml of 2-propanol (see Experimental Section). [b] The ratio observed for acetophenone in several runs permits a claim of at least 2–3% reproducibility. [c] 79% of starting ketone present in the reaction mixture. [d] 50% of starting ketone present in the reaction mixture. [e] From ref 1 (isotope dilution technique). [f] 15% of starting ketone present in the reaction mixture. [g] An essentially quantitative amount of starting ketone present in the reaction mixture.

Relative to unsubstituted acetophenone, the observed ratios of *dl*- to *meso*-pinacols increase or decrease with the corresponding electron-releasing facility of the *para* substituent, decreasing to a point of reversing the predominant diastereomer when the strongly electron-withdrawing trifluoromethyl group is employed.

It is perhaps worth noting that this is the first report of the photopinacolization of the *p*-trifluoromethyl derivative. Unsuccessful attempts to photopinacolize the *p*-hydroxy and *p*-nitro compounds have previously

---

(1) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).

(2) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 291 (1968).

(3) Integration of the total aromatic proton area provided a measure of 100% yield since only the ketonic reactant possessed aromatic protons and quantitative handling should ensure no loss of these irrespective of the path or paths the reaction had taken. Comparison of the total methyl protons of the pinacols with the sum of the aromatic protons, after suitable normalizing, provided the corresponding total yield of the pinacols. The *dl/meso* ratio, in turn, was determined by a peak height comparison of the two methyl proton peaks.

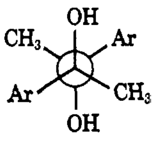
(4) This method of assignment has been previously employed: J. H. Stocker, *J. Am. Chem. Soc.*, **88**, 2878 (1966).

(5) Nmr data have been reported for only one set of diastereomeric pinacols, those derived, as here, from acetophenone: H. Agahigian, J. F. Moraveck, and H. Gauthier, *Can. J. Chem.*, **41**, 194 (1963). Our assignments are in complete accord with theirs.

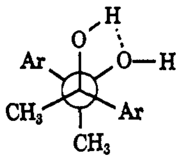
been reported by Heindel,[6] who has also pointed out[7] that the successful pinacolization of *para*-substituted acetophenones appeared to be limited to those with Hammett σ_p values between approximately +0.25 and −0.25. The corresponding value for the trifluoromethyl group[8] is +0.55.

The fact that several of the *para*-substituted acetophenones do not photopinacolize, or do so only in very low yield, may be attributed to a lower lying triplet π,π^* state which is resonance stabilized and is reached by an internal conversion process from the n,π^* triplet.[9,10] The differences, in electronic structure, between the π,π^* and n,π^* triplets are manifested in their chemical behavior. The localization of a nonbonded electron on the carbonyl oxygen in the n,π^* triplet allows H-atom abstraction and subsequent dimerization to the pinacol, whereas the delocalized electrons of the π,π^* triplet cause the carbonyl oxygen to be ineffective as an H-atom abstractor. The unique behavior of the trifluoromethyl group is quite likely due to its inability to participate in other than an inductive fashion.

It has been proposed previously[11] that the intermediate coupling ketyl radicals approach and bond formation take place either without hydrogen bonding (A, *meso* form results) or with such bonding (B, one of two possibilities, *dl* form results). The ratio for acetophenone provides a measure of the relative importance of these two pathways. Substitution on the phenyl ring with an electron-releasing group would be expected to enhance the electron availability or the bridging oxygen for the adjacent hydroxylic proton. This would make B more attractive relative to A and be reflected in an increase in the *dl*/*meso* ratio. Similarly, electron-withdrawing groups should decrease the electron availability on the bridging oxygen and produce a decrease in the *dl*/*meso* ratio. The observed results correlate well with this reasoning.



A, *meso*



B, *dl*

Experimental Section

The starting materials were commercially available research grade chemicals and were used as received. Sample preparation and the apparatus have been previously described.[1] After irradiation, the reaction mixture was added to 100 ml of ether, washed with 50 ml of Na_2CO_3 solution and two 50-ml portions of water, and then dried over anhydrous magnesium sulfate. A suitable aliquot of the ether solution was evaporated to dryness and dissolved in $CDCl_3$, from which solution the nmr spectra were then obtained.

***meso*-2,3-Di(*p*-trifluoromethylphenyl)-2,3-butanediol,** mp 119–120°, was isolated by concentration of the reaction mixture to an oil and subsequent crystallization from hot heptane. It was identified by its infrared (characteristic CF_3 bands between 1065 and 1180 cm^{-1}) and nmr spectra.

Anal. Calcd for $C_{18}H_{16}O_2F_6$: C, 57.14; H, 4.27. Found: C, 56.98; H, 3.98.

Registry No.—*meso*-2,3-Di(*p*-trifluoromethylphenyl)-2,3-butanediol, 14734-18-0.

Acknowledgment.—Financial support of this research under Atomic Energy Commission Contract No. At-(40-1)-2833 (ORO-2833-14) is gratefully acknowledged. The nmr instrument employed, an A-60 (Varian Corp.), was awarded to Louisiana State University in New Orleans by the National Science Foundation under GP-3674.

---

(6) N. D. Heindel, Ph.D. Thesis, University of Delaware, 1963; University Microfilms, Inc., Ann Arbor, Mich., 64-2206, p 100.

(7) See ref 6, p 118.

(8) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(9) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(10) N. D. Heindel, *J. Heterocyclic Chem.*, **3**, 379 (1966).

(11) For considerably greater detail than presented here, *cf.* ref 2.

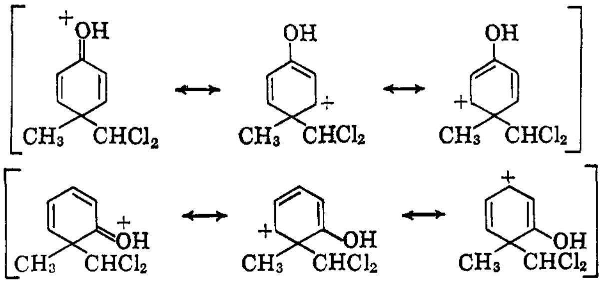
The Nuclear Magnetic Resonance and Ultraviolet Spectra of Some Neutral and Protonated Cyclohexadienones

EDWIN C. FRIEDRICH

Department of Chemistry, University of California, Davis, California 95616

Received June 28, 1967

In 1960, Budzikiewicz[1] reported that the simple "Abnormal Reimer–Tiemann" cyclohexadienones, 4-methyl-4-dichloromethylcyclohexa-2,5-dienone (I) and 6-methyl-6-dichloromethylcyclohexa-2,4-dienone (IV), could be dissolved in concentrated sulfuric acid and recovered quantitatively by dilution with water. The ultraviolet spectra of these dienones in sulfuric acid were interpreted as indicating the formation of "delocalized ions." These must be oxygen-protonated species with structures which may be represented as hybrids of the resonance forms shown.



Recently, in connection with another problem, we have prepared both of the dienones examined by Budzikiewicz as well as all of their possible monomethylated derivatives. We now wish to report an investigation of the ultraviolet and nuclear magnetic resonance spectra of these dienones both in neutral solvents and in concentrated sulfuric acid. This was done in an attempt to learn more about the structures and charge distribution of the delocalized ions formed in sulfuric acid from the dienones.

The simple dienones (I and IV) needed for this study were prepared by method III of von Auwers and Keil[2] which involves the slow addition at reflux temperatures of 45% aqueous sodium hydroxide to a

---

(1) H. Budzikiewicz, *Tetrahedron Letters*, 12 (1960).

(2) K. von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902).